REEY characteristics in hydrothermal gangue carbonates within the sediment-hosted Nkana-Mindola Cu-Co deposit (Zambia) and in two polymetallic vein-type deposits (Kipushi and Dikulushi, Democratic Republic of Congo).

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Abstract. The Central African Copperbelt is a world-class metallogenic province characterized by sediment-hosted stratiform Cu-Co ore deposits and polymetallic vein-type deposits. This project investigates the rare earth element and yttrium (REEY) compositions of the hydrothermal gangue carbonates associated with these mineralizations. In the Nkana-Mindola Cu-Co deposit, layer-parallel to irregular veins display variable REEY patterns, which can be explained by interaction with different sources and varying amounts of remobilization. The uniform REEY composition in the late massive mineralizations at Nkana-Mindola likely reflects similar sources and physicochemical conditions. Their heavy rare earth element (HREE) enrichment is inherited from their sources or generated during precipitation of a light rare earth element (LREE)-selective mineral phase. In the vein-type Kipushi deposit, Fe- and REEY-poor dolomites display upward-convex REEY-patterns while REEY- and Fe-rich dolomites show square-root shaped patterns with prominent negative Eu-anomalies. Both cement phases are closely associated with the main mineralization phase, and likely reflect interaction with different sources at distinct physicochemical conditions. This bimodality is absent at the polymetallic Dikulushi deposit, where the REEY in the Cu-Ag phase are likely remobilized from the earlier Cu-Pb-Zn-Fe phase.

REE, hydrothermal, fluid-rock interaction

1 Introduction

The Neoproterozoic Central African Copperbelt, located at the border between Zambia and the Democratic Republic of Congo (DRC), is the world's richest sediment-hosted Cu-Co province. It contains about 200 Mt of copper (Cailteux et al. 2005) and over 8 Mt of cobalt (Misra 2000) in stratabound deposits alongside other metals (e.g., Pb, Zn) in vein-type deposits. The latter are generally thought to be leached from the continental basement rocks by multiple pulses of hot, saline fluids migrating upward through the Precambrian basement along permeable, fractured zones (Selley et al. 2005; Heijlen et al. 2008). With regard to the sediment-hosted Cu-Co deposits, most recent papers propose a multiphase mineralization (Selley et al. 2005; Cailteux et al. 2005; Dewaele et al., 2006; El Desouky et al. 2009; Muchez et al. 2010). The Cu-Co mineralizing fluids are thought to leach their metals from the basement or the overlying siliciclastics, after which interaction with either reducing sediment layers rich in organic matter or hydrocarbon reservoirs resulted in metal-sulfide precipitation (Annels 1989; Selley et al. 2005; Muchez et al. 2008).

This project seeks more insight into the nature and evolution of the fluids responsible for the mineralizations, by comparing the REEY composition of hydrothermal gangue carbonates in both the Nkana-Mindola Cu-Co deposit (Zambia) and in two polymetallic vein-type deposits at Kipushi and Dikulushi (DRC).

2 Geological context

2.1 The Central African Copperbelt

The Copperbelt deposits are hosted by the Katanga Supergroup, a Neoproterozoic sedimentary sequence mainly deposited between < 880 Ma and ca. 573 Ma (Armstrong et al. 2005; Master et al. 2005). The Katanga basin that contains this supergroup is generally considered to be part of a failed intracontinental rift (e.g., Clemney 1974; Porada and Berhorst 2000). The Roan Group forms the base of the Katanga Supergroup and hosts the majority of mineralizations. It consists of siliciclastic and carbonate sequences which record the transition from a continental rift basin to a Red Sea-type proto-ocean with predominantly dolomitic shales in the Upper Roan and the overlying Nguba Group (Clemney 1974). Convergence between the Congo and Kalahari cratons during the Lufilian Orogeny between 590 and 530 Ma (Rainaud et al. 2005) resulted in closing of this basin, folding and predominantly northward displacement of nappes, generating the Lufilian Fold-and-Thrust Belt currently present as a northward convex arcuate belt measuring 150 by 700 km. The Zambian Nkana-Mindola mine is located near the southeastern edge of this arcuate belt, while the Congolese Kipushi and Dikulushi deposits are located roughly 125 km northward of Nkana-Mindola and in the Lufilian foreland, about 250 km north of the Lufilian arc, respectively.

2.2 Nkana-Mindola deposit (Cu-Co)

At Nkana-Mindola, mineralization occurs in layer-parallel veins (LPV), which record supra-lithostatic pressures at the onset of basin inversion during the

Lufilian orogeny near peak metamorphic conditions at ca. 450 °C and 0.2 GPa (Brems et al. 2009; Muchez et al. 2010). At this stage, fluid migration is thought to be dominantly lateral, originating from the deeper parts of the Katanga sedimentary basin, although a vertical component of fluid flow originating from the basement is also possible. Isotopic evidence indicates that irregular veins reflect remobilization during the Lufilian deformation of earlier formed mineralization in layer-parallel veins (Brems et al. 2009; Muchez et al. 2010). Relatively undeformed massive veins crosscut all earlier mineralizations and likely represent a new fluid input originating from the basement (Muchez et al. 2010).

2.3 Kipushi deposit (Cu-Pb-Zn-Fe)

The vein-type Cu-Pb-Zn-Fe mineralization at Kipushi in the southeastern part of the Copperbelt is mainly hosted by carbonate and to a lesser extent by siliciclastic rocks, which underwent regional metamorphism at low-grade greenschist conditions (Heijlen et al. 2008). This post-orogenic mineralization was dated at 451 Ma (Schneider et al. 2007) and occurred when a metalliferous brine came in contact with a reducing hydrocarbon reservoir, as indicated by the occurrence of relict organic matter and a sulfur isotopic composition indicative for thermochemical sulfate reduction. The main Zn-Cu-(Ge, Pb) sulfide mineralization phase precipitated from a high temperature - high salinity fluid (290-380°C; 30-43 eq. wt% NaCl), while a late mineralization phase occurred at lower temperature and moderate to high salinity (<80-170°C; 23-31 eq. wt% NaCl; Heijlen et al. 2008).

2.4 Dikulushi deposit (Cu-Pb-Zn-Fe + Cu-Ag)

The Cu-Pb-Zn-Fe mineralization at Dikulushi originated from a moderately saline - medium temperature fluid (20-25 eq. wt% NaCl; 100-200°C). A second Cu-Ag mineralization phase likely represents a remobilization of the first phase, whereby mineralization results from mixing of a moderately saline fluid (>19 wt% NaCl eq.) with a low salinity fluid (3 wt% NaCl eq.) in thermal equilibrium with their host rocks at ca. 65 °C (Haest et al. 2009).

3 Results

3.1 Nkana-Mindola deposit (Cu-Co)

Figure 1 reveals that the layer-parallel and irregular veins at Nkana South generally have lower La/Lu ratios compared to their counterparts at Nkana Central and display either relatively flat HREE transects or enrichments towards the HREE. Significant Eu-anomalies are absent in REE-poor LPV, whereas the REEY-rich veins display negative Eu-anomalies.

The nodule and layer-parallel veins at Mindola and Nkana-Central are relatively REE-poor and show upward-convex UCC-normalized patterns with pronounced positive Eu-anomalies. However, the LPV patterns at Nkana-Central show negative Ce-anomalies and lower La/Lu ratios compared to the Mindola nodule.

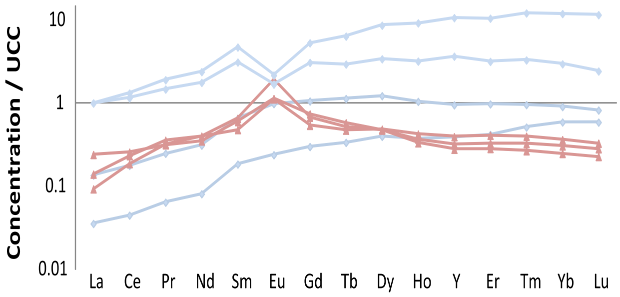

Figure 1. Upper Continental Crust (UCC)-normalized REEY patterns of 6M HCl leachates from nodules and layer-parallel veins at Mindola and Nkana Central (triangles), layer-parallel and irregular veins at Nkana South (diamonds). Analyzed with ICP-MS; UCC composition from Rudnick and Gao (2003).

The massive veins displayed in Figure 2 are generally characterized by low La/Lu ratios, negative Eu-anomalies and a distinct HREE enrichment. Compared to layer-parallel and irregular veins, their REEY-patterns show less variability and their REE-content is generally higher (∑REE 43-75 ppm), except when compared to the REE-richest LPV (∑REE ~150 ppm). Two REE-poor massive veins (∑REE ~25 ppm) show positive Eu-anomalies and lack the HREE enrichment found in all other massive veins.

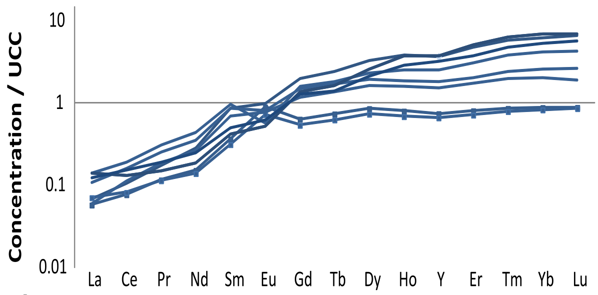

Figure 2. Upper Continental Crust (UCC)-normalized REEY patterns in the massive vein carbonates at Nkana (squares or unbroken lines). Analyzed with ICP-MS; UCC composition from Rudnick and Gao (2003).

3.2 Kipushi deposit (Cu-Pb-Zn-Fe)

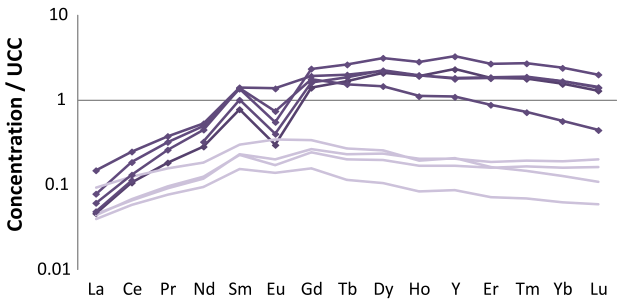

Figure 3. Upper Continental Crust (UCC)-normalized REEY patterns of the Kipushi carbonates. The Fe-poor and Fe-rich dolomite cements are represented by unbroken lines and diamonds respectively. Analyzed with ICP-MS; UCC composition from Rudnick and Gao (2003).

As shown in Figure 3, the gangue dolomites at Kipushi exhibit bimodal REEY patterns: on one hand, Fe-poor dolomite cement displays upward-convex REEY-patterns with relatively low REE contents (avg. ∑REE 15 ppm) and small negative Eu-anomalies. In contrast, the Fe-rich dolomite phase shows square root-like REEY-patterns with a total REE content between 46 and

75 ppm, generally associated with pronounced negative Eu anomalies.

3.3 Dikulushi deposit (Cu-Pb-Zn-Fe + Cu-Ag)

Figure 4 shows that the dolomite and especially the calcite associated with the Cu-Pb-Zn-Fe mineralization are characterized by extremely high REEY-concentrations, with ∑REE between 94 and 757 ppm. The calcite associated with the Cu-Ag mineralization displays REEY patterns similar to the preceding calcite cement, yet contains less REE (∑REE 41-74 ppm).

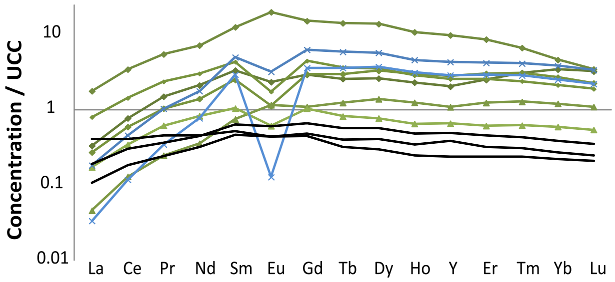

Figure 4. Upper Continental Crust (UCC)-normalized REEY patterns in calcite (diamonds) and dolomite (crosses) associated with the Cu-Pb-Zn-Fe mineralization phase at Dikulushi. The triangles represent the calcite cement associated with the Cu-Ag phase while the unbroken lines correspond to 6M HCl leachates of the Gombela dolomite hosting the mineralization. Analyzed with ICP-MS; UCC composition from Rudnick and Gao (2003).

4 Discussion

4.1 Nkana-Mindola deposit (Cu-Co)

At Nkana South, the REE-rich layer-parallel vein (LPV) signatures shown in Figure 1 are similar to the ones of the REE-poor LPV. This suggests that their higher REE concentrations relate to fluids with higher REE/(Ca+Mg) ratios or less prominent kinetic effects during crystallization, rather than to a difference in source composition. The presence of negative Eu-anomalies in the REE-rich veins can probably be explained by preferential loss of fluid-mobile divalent Eu during subsequent fluid pulses and remobilization.

In contrast, the LPV and the nodule at Nkana Central and Mindola display positive Eu-anomalies. The latter are typical for hydrothermal carbonates and are commonly explained by less efficient sorption and differences in complexation behavior between thermochemically reduced Eu^{2+} and the trivalent REE (e.g., Allwood et al. 2010). The negative Ce-anomalies in the LPV at Central could indicate interaction with their host rocks under oxidizing conditions or inheritance from a marine fluid (cf. Fernández-Nieto et al. 2003). The higher La/Lu ratio in the Mindola nodule compared to the LPV likely relates to its high hydrothermal muscovite content and suggests some extent of equilibration between its parent fluid and the clay-rich dolomitic siltstone host.

Most massive veins in Figure 2 display similar REEY patterns characterized by low La/Lu ratios, an increasing HREE trend and negative Eu anomalies. These similarities suggest near-identical sources and physicochemical conditions for these mineralizations. Two REE-poor massive veins with flat HREE transects and positive Eu-anomalies possibly belong to a different mineralization phase.

Those hosted by the ore shale and the footwall sandstone display similar REEY patterns, indicating that interaction with their host rocks did not affect their REEY signature significantly. Moreover, the similar REEY composition in massive veins at Nkana South and Mindola, about 14 km apart, indicates that their REEY characteristics are representative for a relatively large area, unlike the patterns in the layer-parallel veins. Precipitation of one or more LREE-selective mineral phases prior to mineralization could explain their LREE-depleted REEY signature and would also result in a relative increase in HREE. The HREE-enrichment in the massive veins could also be inherited from their sources, for instance the HREE-enriched anorogenic granites in the basement below the Zambian Copperbelt (cf. Katongo et al. 2004). Preferential complexation of HREE in the mineralizing brine seems unlikely since Cl^- and F^- preferentially complexate the LREE (Migdisov et al. 2009) and these are probably important ligands in Cl-rich hydrothermal brines (Kučera et al. 2009).

4.2 Kipushi deposit (Cu-Pb-Zn-Fe)

The two REEY pattern types in Figure 3 correspond to the Fe-poor and Fe-rich dolomite cements respectively. Although both dolomite phases are probably closely associated with the main high temperature - high salinity mineralization phase (Chabu 1995; Heijlen et al. 2008), physicochemical conditions in both hydrothermal fluids are not necessarily similar. For instance, the difference in Fe-content probably relates to a different oxidation potential in the hydrothermal brines. At oxidizing conditions, Fe is mostly trivalent and therefore immobile in hydrothermal fluids (e.g., Fernández-Nieto et al. 2003). Because changes in the oxidation potential most likely do not influence the mobility of normally trivalent REE at hydrothermal conditions (e.g., Wood et al. 1990; Haas et al. 1995), the two distinct REEY patterns in the fluids are interpreted to reflect interaction with different sources at distinct physicochemical conditions.

4.3 Dikulushi deposit (Cu-Pb-Zn-Fe + Cu-Ag)

The carbonates associated with the Cu-Pb-Zn-Fe phase are extremely REEY-rich, indicating mineralizing fluids with high REE/[Ca (+Mg)] ratios, likely related to physicochemical conditions favorable for REE mobilization. The variable Eu-anomalies in the calcite likely reflects variable redox conditions during mineralization and remobilization. Surprisingly, the distinct geochemistry of the two mineralization phases (Cu-Pb-Zn-Fe and Cu-Ag) is not reflected in the REEY patterns. The latter supports the hypothesis from Haest et al. (2009), who interpreted the Cu-Ag mineralization phase as a remobilization of the earlier Cu-Pb-Zn-Fe phase. In this scenario, the lower REEY-concentrations likely reflect less efficient REE mobilization at the lower salinities and temperatures resulting from this mixing.

Acknowledgements

We are grateful to dr. Elvira Vassilieva, dr. Stijn Dewaele, dr. Hamdy El Desouky and drs. Jorik Van Wilderode for stimulating discussions on the geochemical analysis, REE geochemistry and metallogenesis of the Copperbelt deposits. David Debruyne and Lieve Balcaen are respectively Research Assistant and Senior Research Assistant of the Fund for Scientific Research – Flanders (FWO-Vlaanderen). This research is also financially supported by the research grant G.A078.11 from FWO-Vlaanderen (Belgium).

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